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ELECTRON IRRADIATION—INDUCED DEFECTS IN p-TYPE SILICON AT 80 K

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Abstract—Using trancient capacitance spectroscopy we determined energy levels and studied the annealing behaviour of defect states introduced by 1.5 MeV electron irradiation of float-zone and pulled boron-doped silicon at 80 K. We found that apart from a previously reported bistable defect attributed to the boron substitutional-vacancy pair, the carbon interstitial in the float-zone silicon and the level $E_v + 0.34$ eV in the pulled silicon exhibit charge-dependent peak amplitudes. Additionally, we found that in pulled silicon the ($E_v + 0.20$ eV) defect level is not only due to the divacancies but also to another kind of contributor which shares it. Finally, some other levels are reported as well.

Keywords: DLTS, silicon, boron, electron-irradiation, metastable, defect.

1. INTRODUCTION

It is well-known that crystalline silicon, apart from the dopant impurity which in our case is boron, inevitably contains oxygen and carbon due to its preparation procedure. Thus, irradiating boron-doped silicon at 80 K we expect to see defects as the vacancy, the divacany, the carbon interstitial and the boron interstitial, etc. which are created immediately after the collision (primary defects). Secondary defects produced by interactions between primary defects or between a primary defect and an imperfection [e.g. the ($B_s - V$) or the ($V - O$)] may be seen as the sample temperature rises and some of the primaries begin to migrate forming pairs and complexes. Additionally, silicon interstitial interactions with impurities [e.g. the ($B_s - Si_i$)] may also be detected if they produce levels in the forbidden energy gap.

The main purpose of this work was the investigation of defects showing charge-state-controlled configurational changes or charge-dependent behaviour. We studied defects which exhibited two metastable configurations [1] by applying the following steps:

(a) The sample is brought to a certain temperature T;

(b) The sample is shorted (with zero reverse bias, $V_R = 0$) and annealed for a time t, to establish the first configuration;

(c) The sample is quenched (with $V_R = 0$) at a low temperature (80 K);

(d) The DLTS (Deep Level Transient Spectroscopy) spectrum is taken without surpassing the annealing temperature T;

(e) In order to create the second configuration, the above procedure is repeated by changing only the applied reverse bias ($V_R = 5$ V) in (b) and (c).

Spectral changes in peaks, when cooling the samples under different bias conditions, are indications of the configuration changes of some defects which result in alterations of their electronic states. Any reduction or enhancement of the peak amplitudes of a defect, due to bias conditions, also provides additional information about the defect itself.

2. THE EXPERIMENTAL PROCEDURE

Schottky diodes were fabricated by evaporation of very pure Al on the surface of boron-doped float-zone and pulled silicon. The specimens were cut by cleaving from silicon wafers given from Wacker. The nominal resistivities were (0.85–1.1) Ω cm for the float-zone and (3–5) Ω cm for the pulled. The oxygen concentration was $\sim 10^{16}$ cm^{-3} for the float-zone and $\sim 10^{18}$ cm^{-3} for the pulled material. Carbon was also present up to levels of $\sim 10^{17}$ cm^{-3}. C (V) profiling revealed uniform acceptor concentrations of 1.7×10^{16} cm^{-3} for the float-zone and 3.8×10^{15} cm^{-3} for the pulled crystals in good agreement with the above resistivities quoted from the manufacturers. The Schottky contact was created in two steps. First, a thin layer of Al was produced which made feasible optical measurements after laser illumination. Then, a thicker layer of Al was produced, covering part of the first, to allow the probe touch for the electrical measurements. C(V) and C(T) tests before irradiation gave almost ideal results. DLTS and MCTS (Minority Carrier Trap Spectroscopy) scans also gave no indication of any surface signal in any of our specimens before irradiation.

The specimens were irradiated in vacuum, at 80 K, with 1.5 MeV electrons at a current of 0.3 μA/cm^2. The 2 MeV Van der Graaff machine of Reading

† The experiment has been carried out at Reading University, England, during a leave of absence.

University (England) was used. The total dose was about 4×10^{16} e/cm^2. We used a home-made, portable, liquid Nitrogen cryostat connected to the DLTS equipment and with provision for *in situ* irradiation. The inability of the system to operate below 80 K prevented studies at very low temperatures.

Transient capacitance spectroscopy (DLTS and MCTS) was our experimental method [2, 3]. This is a widely used method for studying defects induced in semiconductors after irradiation. According to this, each defect gives rise to a certain peak in the spectrum (positive for majority and negative for minority traps), at a certain temperature. Twelve rate windows (r.w.) were available, operating between 0.4 and 2500 s^{-1}. Capture cross sections were determined by varying the pulse width and measuring the corresponding height of the peak. The limit of our equipment for the pulse width was about 0.5 μs; below this value the pulse was not square and the results were not reliable. The given values for the capture cross sections were measured at the temperature where we had the signal in the spectrum. No correction was made for any temperature dependence of the capture cross sections. The reported activation energies for carrier emission are accurate to about ± 0.02 eV.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. *Float-zone silicon*

After irradiation, the first scans were taken at temperatures below 155 K where the vacancy begins to migrate. Three main defects have been detected in this region, as was expected: the vacancy, the divacancy ($E_v + 0.21$ eV) and the carbon interstitial ($E_v + 0.29$ eV). At the minimum achievable temperature of 80 K the vacancy was detected only with the two fastest available rate windows operating at 1000 and 2500 s^{-1}. The use of only two rate windows does not allow the determination of the exact activation energy. However, the position of the peak on the temperature axis and the annealing behaviour are consistent with the level ($E_v + 0.13$ eV) of the vacancy [4].

The next step was annealing at 215 K for about 30 min under zero bias. The time was long enough for the vacancy to migrate and two new peaks of about the same amplitude appeared in the DLTS spectrum in the extended temperature region: peak A_1 with energy ($E_v + 0.32$ eV) and peak A_2 with energy ($E_v + 0.37$ eV) (Fig. 1). After annealing at 215 K under $V_R = 5$ V the DLTS spectrum shows that these two peaks decay simultaneously while another peak B_1 is rising. This new peak can be seen only partially when using the fastest available rate window. Thus, its energy cannot be specified.

The regeneration of the A_1 and A_2 peaks can be achieved by annealing with the bias off. We can correspondingly regenerate B_1 with the bias on. These three peaks have been studied recently [5] and

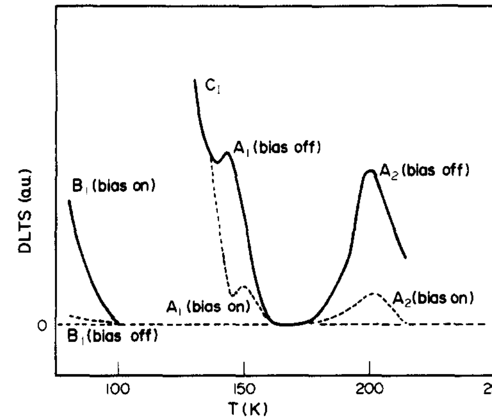

Fig. 1. DLTS spectra of the two metastable configurations in boron-doped float-zone silicon; r.w. = 0.4 s^{-1} for configuration A (solid curve with bias off, dashed curve with bias on); r.w. = 2500 s^{-1} for configuration B (solid curve with bias on, dashed curve with bias off).

there is strong evidence that A_1 and A_2 are the manifestations of configuration A of a bistable defect while B_1 is the manifestation of its alternate configuration B. Even if another level exists for configuration B_1 this has not been detected in this study either because it gives a trace below the 80 K temperature limit of our equipment, or because it can not be traced by DLTS [1].

In Fig. 1 we give the two DLTS spectra that characterize the metastable configurations (r.w. = 1 s^{-1}).

In Fig. 2 the annealing behaviour of A_1 and A_2 is depicted under zero and 5 V reverse bias (r.w. = 1 s^{-1}). A characteristic bias dependence of the peak amplitude of the carbon interstitial is also depicted. The concentration of the carbon interstitial is higher under zero bias than under reverse bias

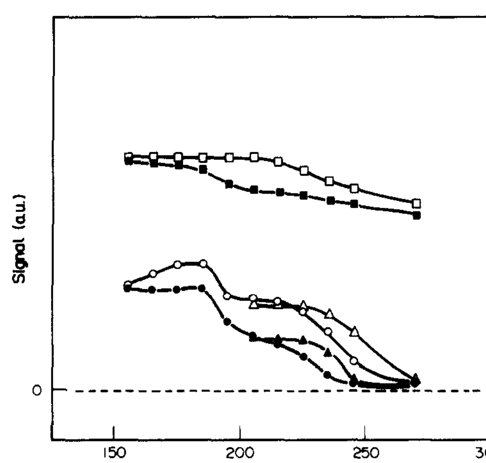

Fig. 2. Five min isochronal annealings under zero (○) and under −5 V reverse (●) bias for H_4. The same for H_5 [(△) under zero bias and (▲) under 5 V reverse bias]. There is also depicted a charge dependence of the carbon interestitial [(□) under zero bias and (■) under 5 V reverse bias, r.w. = 1 s^{-1}]

conditions in these Schottky diodes of p-type material. The opposite has been reported for a diffused diode and an implanted diode of n-type silicon [6].

The boron substitutional-vacancy complex ($B_s - V$) seems to be a very strong canditate for the levels A_1, A_2 and B_1. The annealing behaviour of A_1 and A_2 is consistent with that reported by Watkins [7] for an EPR spectrum labelled Si-G10 which he tentatively associated with the above complex. The fact that these levels do not appear in pulled silicon, as we shall see later, is also consistent with the above identification. Oxygen is known to be an effective trap for vacancies and in the pulled crystal with the oxygen concentration about two orders of magnitude larger than the boron concentration most of the vacancies would be trapped by oxygen.

It is understood that a complete study of the ($B_s - V$) complex requires DLTS measurements in the temperature range below 80 K in order to see the whole spectrum. A repetition of the measurements with another chemical acceptor of the same group as boron, e.g. aluminum or galium, would be useful for the sake of comaprison. EPR, TSCAP and photoionization measurements are also needed to verify and complete, if necessary, the proposed model [5] which has been concluded from DLTS experiments.

3.2. *Pulled silicon*

For the same reasons as in float-zone silicon the first scans were kept below 155 K. The vacancy and the carbon interstitial appear as expected. However, some other noteworthy facts have been observed. Figure 3 shows two DLTS spectra in the above region taken with the fastest available rate window of $2500\,s^{-1}$ (the carbon interstitial does not appear in this spectrum because it has a trace beyond 155 K). The first spectrum (dashed line) has been taken immediately after the irradiation and the second (solid line) ~ 1 h later. We adopted a labelling system for the observed peaks compatible with and

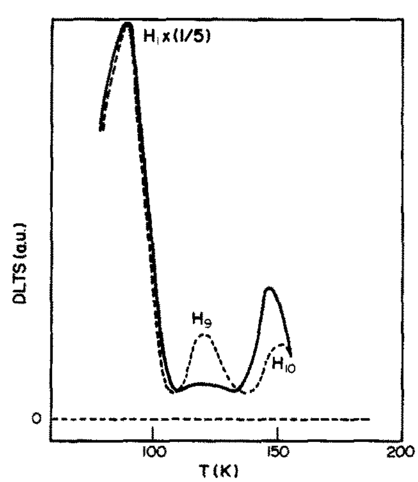

Fig. 3. The DLTS spectrum of pulled, boron-doped silicon below 155 K. Dashed curve immediately after the irradiation. Solid curve ~1 h later (r.w. = $2500\,s^{-1}$).

an extension of that in Ref. [5]. The peak labelled H_9 decays quickly but does not vanish completely. It stabilizes at a low concentration (about 10% of its initial value) giving an energy of $E_v + 0.15$ eV. At the same time the peak labelled H_{10} increases its amplitude and shows a small shift to the lower temperature giving an energy of $E_v + 0.20$ eV. The increase in H_{10} is about the same as the decrease in H_9.

All the evidence from H_{10}, e.g. its position with temperature, its relative concentration and the annealing behaviour, are consistent with the divacancy. Moreover the obvious connection of H_{10} with H_9 points out that something else also participates in the formation of H_{10}. An increase of the divacancy concentration upon heating from 140 K and below has been reported in low temperature neutron-irradiated silicon [8]. It was suggested there, that the neutron-induced cluster of defects is a vacancy-rich region which begins to reorder with increasing temperature. We cannot propose the same explanation here since electron irradiation with moderate energy (1.5 MeV) at low temperatures (80 K) produces simple defects without introducing clusters and disordered regions [9].

The available information is obviously inadequate to identify H_9. However, we know that below 150 K the vacancy is still immobile [10]. Thus, it is reasonable to make associations of secondary defects (if that is the case for H_9) of silicon interstitial interactions with impurities (e.g. $Si_i^+ + O \rightarrow Si_i^+O$ or $Si_i^+ + B_s^- \rightarrow Si_i^+ B_s^-$). Such interactions have been considered by Vavilov *et al.* [11] who studied defects in silicon created by a 2 MeV electron irradiation at 80 K; their method employed measurements of the Hall constant and conductivity of the IR absorption spectra and of the minority carrier diffusion length.

It is worth noticing that when we repeated our experiment with half the dose (1.7×10^{16} e/cm^2) and half the beam current ($0.15\,\mu A/cm^2$) some remarkable changes appeared in the DLTS spectrum. Although the vacancy and the carbon interstitial appear quite similar as before with small alterations in their concentration due to the different conditions of irradiation, there is no evidence of H_9 and H_{10}. A new level with energy ($E_v + 0.13$ eV) appears with a peak height comparable to that of H_{10}. A similar level ($E_v + 0.12$ eV), determined by the thermally stimulated capacitance technique, is also discussed by Brabant *et al.* [12]. They discuss its association with the divacancy but they leave open any identification because of the value of the activation energy. More work is needed here to study the influence of the beam current and the irradiation conditions in general to the production of defects.

In the second step we annealed the sample at 215 K for about 30 min. After the vacancy had completely vanished, H_{10} shows an increase of its concentration of about 16%, which is consistent with the association of H_{10} with the divacancy. Two new peaks now appear in the extended temperature region, H_{11}

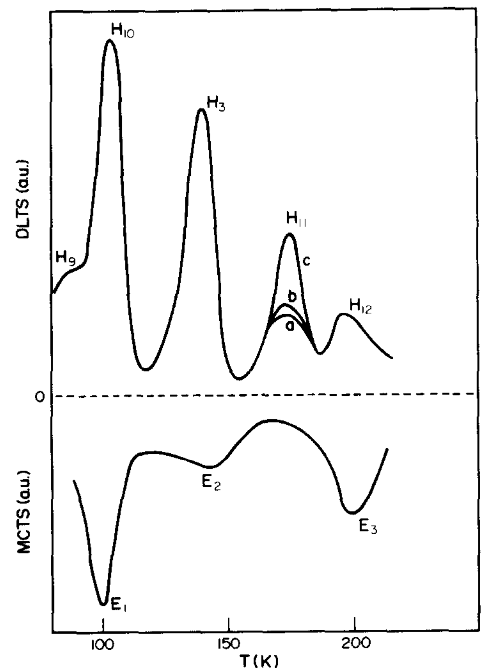

Fig. 4. The DLTS and MCTS spectra of pulled, boron-doped Si after the annealing out of the vacancy (r.w. = $1\,s^{-1}$). (a) H_{11} under $V_R = 5$ V for $V_f = 0$ V and $V_f = 1.2$ V; (b) H_{11} under $V_R = 0$ V for $V_f = 0$ V; (c) H_{11} under $V_R = 0$ for $V_f = 1.2$ V.

with energy ($E_v + 0.34$ eV) and H_{12} with energy ($E_v + 0.38$ eV). The concentration of H_{12} was very low under the experimental conditions (dose = 1.7×10^{16} e/cm^2, $j = 0.15\,\mu$A/cm^2).

Figure 4 shows the whole DLTS and MCTS spectrum after the vacancy has been annealed out. Detailed measurements were taken to examine any charge dependent behaviour displayed in the spectrum. For a filling pulse amplitude $V_f = 0$ V during the DLTS scan, the peak amplitude of H_{12} shows small changes after annealing at 215 K under zero and under 5 V reverse bias according to the procedure mentioned previously. For a filling pulse amplitude $V_f = 1.2$ V (just above the built-in potential of the specimen after the irradiation) the peaks show a much greater difference for zero and 5 V reverse bias annealings. For the intermediate values of V_f, the larger the filling pulse amplitude the greater the peaks height difference. The fact that the above changes of V_f affect very slightly the heights of all the other present peaks is sufficient indication that H_{11} shows a certain profile, characteristic of its nature. This behaviour of H_{11} is the same for all rate windows which are slow enough to give a trace of it below 200 K. For faster rate windows the peak amplitude difference begins to decrease. The application of the procedure for the detection of metastable configurations did not show any other peak to rise under the conditions of annealing with 5 V reverse bias when H_{11} decays. However, due to the lack of any information below 80 K, we cannot draw any final conclusion.

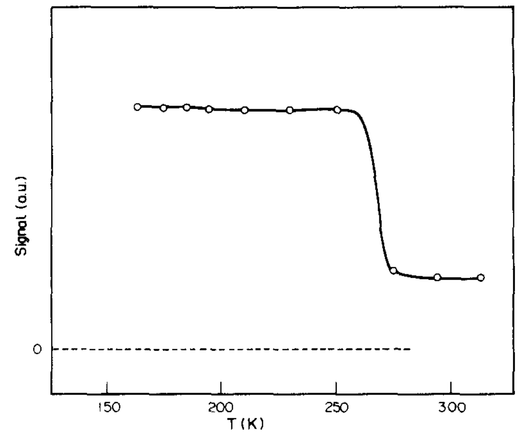

Fig. 5. Twenty-five min isochronal annealings under zero bias for H_{11} (r.w. = $1\,s^{-1}$, $V_f = 1.2$ V).

Figure 5 shows 25 min isochronal annelaings of H_{11} under 0 V bias conditions ($V_f = 1.2$ V). In this Fig. the regeneration of H_{11} vs temperature is exhibited. Beyond 270 K, H_{11} stabilizes at a low concentration and keeps its presence for some hours at room temperature. A capture cross section analysis gave for H_{11}, $\sigma = 8 \times 10^{-19}$ cm^2 on average.

A DLTS spectrum for diffused silicon diodes (boron concentration: 1.5×10^{14} cm^{-3}) after 1 MeV electron irradiation (dose: 2.8×10^{15} e/cm^2), at 77 K, is reported by Kimerling *et al.* [13]. They did not refer to H_{11} and H_{12} either because they did not take the spectrum in the extended temperature region after the annealing of the vacancy or because they restricted themselves below 200 K in the temperature axis and they used a rate window ($555\,s^{-1}$) which can trace these defects at higher temperatures.

Finally, we report three minority traps in the MCTS spectrum (Fig. 4): E_1 with energy $E_c - 0.18$ eV which may be taken as the A centre; E_2 with energy $E_c - 0.24$ eV and E_3 with energy $E_c - 0.46$ eV. E_3 has been seen in float-zone and pulled silicon after irradiation at room and liquid nitrogen temperature and it might be correlated with one of the manifestations of the divacancy.

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